

500 Rec'd PCT/PTO 23 JUL 2001

FORM PTO-1590
(REV 12-29-99)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

BDL-352XX

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/889862

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 36 U.S.C. 371INTERNATIONAL APPLICATION NO.
PCT/FR00/03276INTERNATIONAL FILING DATE
24 November 2000PRIORITY DATE CLAIMED
24 November 1999

TITLE OF INVENTION

A METHOD OF MANUFACTURING A THERMOSTRUCTURAL COMPOSITE MATERIAL BOWL, A BOWL AS
OBTAINED BY THE METHOD, AND USE OF THE BOWL AS A CRUCIBLE SUPPORT

APPLICANT(S) FOR DO/EO/US

JEAN-MICHEL GUIRMAN; DOMINIQUE COUPE; JEAN-MICHEL GEORGES

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
 - ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:
 - FORMAL DRAWINGS (6 sheets)
 - VERIFICATION OF TRANSLATION

Express Mail Number

EL 751779451 US

U.S. APPLICATION NO. (if known, see 37 CFR 1.5) 09/889862	INTERNATIONAL APPLICATION NO PCT/FR00/03276	ATTORNEY'S DOCKET NUMBER BDL-352XX
---	--	---------------------------------------

17. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1,000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00	CALCULATIONS PTO USE ONLY
---	---

ENTER APPROPRIATE BASIC FEE AMOUNT =	\$ 860.00
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	\$ 0

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	54 - 20 =	34	X \$18.00	\$ 612.00
Independent claims	2 - 3 =	0	X \$80.00	\$ 0
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				\$ 0
TOTAL OF ABOVE CALCULATIONS =				\$1,472.00
Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$ --
SUBTOTAL =				\$1,472.00
Preprocessing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$ 0
TOTAL NATIONAL FEE =				\$1,472.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				\$ 40.00
TOTAL FEES ENCLOSED =				\$1,512.00
				Amount to be Refunded: \$
				Charged: \$

a. ☒ A check in the amount of \$ 1,472.00 to cover the above fees is enclosed. A check in the amount of \$40.00 is enclosed for the assignment recordation fee.

b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 23-0804. A duplicate copy of this sheet is enclosed.


NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

Customer Number 207

SEND ALL CORRESPONDENCE TO:

Weingarten, Schurgen, Gagnebin & Hayes LLP
 Ten Post Office Square
 Boston, Massachusetts 02109

Date: 7-23-01


 SIGNATURE
 Charles L. Gagnebin III
 NAME
 25,467
 REGISTRATION NUMBER

09/889862

JC18 Rec'd PCT/PTO ^{PATENT} 23 JUL 2001IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application : JEAN-MICHEL GUIRMAN, ET AL.
 Application No. :
 Filed : Herewith
 For : A METHOD OF MANUFACTURING A
 THERMOSTRUCTURAL COMPOSITE MATERIAL
 BOWL, A BOWL AS OBTAINED BY THE METHOD,
 AND USE OF THE BOWL AS A CRUCIBLE
 SUPPORT
 Examiner :
 Attorney's Docket : BDL-352XX

Group Art Unit:

 I hereby certify that this correspondence is being deposited
 with the United States Postal Service as first class mail in an
 envelope addressed to: Commissioner for Patents, Washington,
 D.C. 20231 on _____.

By: _____
 Charles L. Gagnebin III
 Registration No. 25,467
 Attorney for Applicant(s)

PRELIMINARY AMENDMENT

BOX PCT
 Commissioner for Patents
 Washington, D.C. 20231

Sir:

Kindly enter the following Preliminary Amendment in the
 above-identified application:

Express Mail Number

EL 751779451 US

In the Claims:

Please amend the Claims to read as follows (a copy of the amended claims showing the additions and deletions appears at the end for the Examiner's convenience):

4/ A method according to claim 2, characterized in that the unidirectional sheets are bonded to one another by knitting a thread which passes from one side of the fabric to the other.

5/ A method according to claim 2, characterized in that the unidirectional sheets are bonded together by needling.

6/ A method according to claim 2, characterized in that the unidirectional sheets are bonded together by stitching with a thread that passes from one side of the fabric to the other.

7/ A method according to claim 2, characterized in that the plies are superposed by being mutually angularly offset around an axis passing through the bottom of the bowl.

9/ A method according to claim 1, characterized in that plies are used formed of carbon fiber yarns that are free of surface functions.

10/ A method according to claim 1, characterized in that plies are used formed of carbon fiber yarns provided with an interphase coating of pyrolytic carbon.

11/ A method according to claim 1, characterized in that the superposed plies are bonded together by needling so as to transfer fibers taken from the plies transversely thereto.

13/ A method according to claim 11, characterized in that the density of fibers transferred transversely relative to the plies is controlled throughout the thickness of the preform.

14/ A method according to claim 1, characterized in that the superposed plies are bonded together by stitching.

15/ A method according to claim 1, characterized in that the superposed plies are bonded together by implanting threads transversely relative to the plies.

16/ A method according to claim 1, characterized in that the preform is consolidated prior to densification.

18/ A method according to claim 1, characterized in that, prior to densification, the preform is subjected to heat treatment for dimensional stabilization and for purification at a temperature lying in the range 1600°C to 2800°C.

19/ A method according to claim 1, characterized in that the preform is densified by chemical vapor infiltration.

20/ A method according to claim 1, characterized in that the deformable two-dimensional fiber plies used are whole, being free from any cutouts or slots, thereby obtaining a preform for a complete bowl in one piece, and densification is performed on the complete bowl preform.

21/ A method according to claim 1, characterized in that the deformable two-dimensional fiber plies used are whole, being free from cutouts or slots, so as to obtain a complete one-piece bowl preform, a hole is made through the bottom of the preform prior to densification of the preform by chemical vapor infiltration, and the hole is subsequently closed by a plug.

22/ A method according to claim 1, characterized in that the deformable two-dimensional fiber plies used are whole, having a

substantially central opening, the plies are superposed on the former so that their openings are in alignment, thereby obtaining a bowl preform with a hole through the bottom of the preform constituted by the aligned openings in the plies, the preform is densified by chemical vapor infiltration, and the hole is subsequently closed by a plug.

23/ A method according to claim 21, characterized in that a plug of thermostructural composite material is used.

24/ A method according to claim 21, characterized in that an additional step of chemical vapor infiltration is performed after the plug has been put into place in the hole formed in the bottom of the preform.

25/ A method according to claim 1, characterized in that after densification, purification heat treatment is performed at a temperature lying in the range 1600°C to 2700°C.

26/ A method according to claim 1, characterized in that after densification, a coating of pyrolytic carbon is formed on the bowl.

27/ A method according to claim 1, characterized in that after densification, a coating of silicon carbide is formed on the bowl.

28/ A method according to claim 21, characterized in that the inside face of the bowl is lined with a protective coating.

32/ A bowl according to claim 30, characterized in that the fiber plies are formed of unidirectional sheets superposed in different directions.

35/ A bowl according to claim 33, characterized in that the matrix is made at least in part out of ceramic.

37/ A bowl according to claim 30, characterized in that at least its inside face is coated in a layer of pyrolytic carbon.

38/ A bowl according to claim 30, characterized in that at least its inside face is coated in a layer of silicon carbide.

39/ The use of a bowl according to claim 30 for supporting a crucible in an installation for producing monocrystalline

silicon ingots, the use being characterized in that a protective layer is interposed between the bowl and the crucible.

Please add the following new claims 41-54:

41/ A method according to claim 3, characterized in that the unidirectional sheets are bonded to one another by knitting a thread which passes from one side of the fabric to the other.

42/ A method according to claim 3, characterized in that the unidirectional sheets are bonded together by needling.

43/ A method according to claim 3, characterized in that the unidirectional sheets are bonded together by stitching with a thread that passes from one side of the fabric to the other.

44/ A method according to claim 12, characterized in that the density of fibers transferred transversely relative to the plies is controlled throughout the thickness of the preform.

45/ A method according to claim 22, characterized in that a plug of thermostructural composite material is used.

46/ A bowl according to claim 31, characterized in that the fiber plies are formed of unidirectional sheets superposed in different directions.

47/ A bowl according to claim 34, characterized in that the matrix is made at least in part out of ceramic.

48/ A method according to claim 3, characterized in that:

the unidirectional sheets are bonded to one another by one of knitting a thread which passes from one side of the fabric to the other, by needling, or by stitching with a thread that passes from one side of the fabric to the other; and

the plies are superposed by being mutually angularly offset around an axis passing through the bottom of the bowl.

49/ A method according to claim 48, characterized in that the superposed plies are bonded together by needling so as to either transfer fibers taken from the plies transversely thereto or with each newly draped ply needled onto the underlying structure; and

the density of fibers transferred transversely relative to the plies is controlled throughout the thickness of the preform.

50/ A method according to claim 48, characterized in that:

the preform is consolidated prior to densification;

the preform is consolidated by being impregnated with a resin, by polymerizing the resin, and by carbonizing the polymerized resin;

prior to densification, the preform is subjected to heat treatment for dimensional stabilization and for purification at a temperature lying in the range 1600°C to 2800°C;

the preform is densified by chemical vapor infiltration;
and

the deformable two-dimensional fiber plies used are whole, being free from any cutouts or slots, thereby obtaining a preform for a complete bowl in one piece, and densification is performed on the complete bowl preform.

51/ A method according to claim 50, characterized in that either the deformable two-dimensional fiber plies used are whole, being free from cutouts or slots, so as to obtain a complete one-piece bowl preform, a hole is made through the bottom of the preform prior to densification of the preform by chemical vapor infiltration, and the hole is subsequently closed by a plug.

52/ A method according to claim 50, characterized in that the deformable two-dimensional fiber plies used are whole, having a substantially central opening, the plies are superposed on the former so that their openings are in alignment, thereby obtaining a bowl preform with a hole through the bottom of the preform constituted by the aligned openings in the plies, the preform is densified by chemical vapor infiltration, and the hole is subsequently closed by a plug;

a plug of thermostructural composite material is used;

an additional step of chemical vapor infiltration is performed after the plug has been put into place in the hole formed in the bottom of the preform;

after densification, purification heat treatment is performed at a temperature lying in the range 1600°C to 2700°C;

after densification, a coating of pyrolytic carbon or silicon carbide is formed on the bowl;

the inside face of the bowl is lined with a protective coating; and

a protective coating is used made of a thermostructural composite material.

53/ A bowl according to claim 36, characterized in that at least its inside face is coated in a layer of pyrolytic carbon or silicon carbide.

54/ The use of a bowl according to claim 53 for supporting a crucible in an installation for producing monocrystalline silicon ingots, the use being characterized in that a protective layer is interposed between the bowl and the crucible, and characterized in that a protective layer of thermostructural composite material is used.

REMARKS

This Preliminary Amendment puts the claims into proper form for examination. Note that claims 4-7, 9-11, 13-16, 18-28, 32, 35, 37-39 have been amended; new claims 41-54 have been added; and claims 1-3, 8, 12, 17, 29-31, 33, 34, 36, and 40 remain unchanged. Kindly calculate the filing fee based on the amended claims.

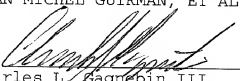
This Application contains a translation of the title and abstract as they were when originally filed by the Applicant. No account has been taken of any changes that may have been made

subsequently by the PCT Authorities acting ex officio, e.g.,
under PCT Rules 37.2, 38.2, and/or 48.3.

The Examiner is encouraged to telephone the undersigned
attorney to discuss any matter which would expedite allowance of
the present application.

Respectfully submitted,

JEAN-MICHEL GUIRMAN, ET AL.

By: 
Charles L. Gagnebin III
Registration No. 25,467
Attorney for Applicants

WEINGARTEN, SCHURGIN, GAGNEBIN
& HAYES LLP
Ten Post Office Square
Boston, MA 02109
Telephone: (617) 542-2290
Telecopier: (617) 451-0313

Date: 7-23-1

CLG/mc/254476-1
Enclosure

Red-Lined claims for the Examiner's convenience:

4/ A method according to claim 2 ~~or claim 3~~, characterized in that the unidirectional sheets are bonded to one another by knitting a thread which passes from one side of the fabric to the other.

5/ A method according to claim 2 ~~or claim 3~~, characterized in that the unidirectional sheets are bonded together by needling.

6/ A method according to claim 2 ~~or claim 3~~, characterized in that the unidirectional sheets are bonded together by stitching with a thread that passes from one side of the fabric to the other.

7/ A method according to ~~any one of claims 2 to 6~~, characterized in that the plies are superposed by being mutually angularly offset around an axis passing through the bottom of the bowl.

9/ A method according to ~~any one of claims 1 to 8~~, characterized in that plies are used formed of carbon fiber yarns that are free of surface functions.

10/ A method according to ~~any one of claims 1 to 8~~,
characterized in that plies are used formed of carbon fiber
yarns provided with an interphase coating of pyrolytic carbon.

11/ A method according to ~~any one of claims 1 to 10~~,
characterized in that the superposed plies are bonded together
by needling so as to ~~transfer~~transfer fibers taken from the
plies transversely thereto.

13/ A method ~~being~~being according to ~~any claim 11 or claim 12~~,
characterized in that the density of fibers transferred
transversely relative to the plies is controlled throughout the
thickness of the preform.

14/ A method according to ~~any one of claims 1 to 10~~,
characterized in that the superposed plies are bonded together
by stitching.

15/ A method according to ~~any one of claims 1 to 10~~,
characterized in that the superposed plies are bonded together
by implanting threads transversely relative to the plies.

16/ A method according to ~~any one of claims 1 to 15~~, characterized in that the preform is consolidated prior to densification.

18/ A method according to ~~any one of claims 1 to 17~~, characterized in that, prior to densification, the preform is subjected to heat treatment for dimensional stabilization and for purification at a temperature lying in the range 1600°C to 2800°C.

19/ A method according to ~~any one of claims 1 to 18~~, characterized in that the preform is densified by chemical vapor infiltration.

20/ A method according to ~~any one of claims 1 to 19~~, characterized in that the deformable two-dimensional fiber plies used are whole, being free from any cutouts or slots, thereby obtaining a preform for a complete bowl in one piece, and densification is performed on the complete bowl preform.

21/ A method according to ~~any one of claims 1 to 19~~, characterized in that the deformable two-dimensional fiber plies used are whole, being free from cutouts or slots, so as to

obtain a complete one-piece bowl preform, a hole is made through the bottom of the preform prior to densification of the preform by chemical vapor infiltration, and the hole is subsequently closed by a plug.

22/ A method according to ~~any one of claims 1 to 19,~~ characterized in that the deformable two-dimensional fiber plies used are whole, having a substantially central opening, the plies are superposed on the former so that their openings are in alignment, thereby obtaining a bowl preform with a hole through the bottom of the preform constituted by the aligned openings in the plies, the preform is densified by chemical vapor infiltration, and the hole is subsequently closed by a plug.

23/ A method according to claim 21 ~~or claim 22,~~ characterized in that a plug of thermostructural composite material is used.

24/ A method according to ~~any one of claims 21 to 23,~~ characterized in that an additional step of chemical vapor infiltration is performed after the plug has been put into place in the hole formed in the bottom of the preform.

25/ A method according to ~~any one of claims 1 to 24~~, characterized in that after densification, purification heat treatment is performed at a temperature lying in the range 1600°C to 2700°C.

26/ A method according to ~~any one of claims 1 to 25~~, characterized in that after densification, a coating of pyrolytic carbon is formed on the bowl.

27/ A method according to ~~any one of claims 1 to 25~~, characterized in that after densification, a coating of silicon carbide is formed on the bowl.

28/ A method according to ~~any one of claims 21 to 27~~, characterized in that the inside face of the bowl is lined with a protective coating.

32/ A bowl according to claim 30 ~~or claim 31~~, characterized in that the fiber plies are formed of unidirectional sheets superposed in different directions.

35/ A bowl according to claim 33 ~~or claim 34~~, characterized in that the matrix is made at least in part out of ceramic.

37/ A bowl according to ~~any one of claims 30 to 36~~,
characterized in that at least its inside face is coated in a
layer of pyrolytic carbon.

38/ A bowl according to ~~any one of claims 30 to 36~~,
characterized in that at least its inside face is coated in a
layer of silicon carbide.

39/ The use of a bowl according to ~~any one of claims 30 to 38~~
for supporting a crucible in an installation for producing
monocrystalline silicon ingots, the use being characterized in
that a protective layer is interposed between the bowl and the
crucible.

Title of the invention

A method of manufacturing a thermostructural composite material bowl, a bowl as obtained by the method, and use of the bowl as a crucible support

Field of the invention

The invention relates to manufacturing hollow parts out of thermostructural composite material, more particularly parts having a deep stamped shape that cannot be developed, that is not necessarily axially symmetrical, with an end wall portion and a side wall portion interconnected by portions in which the radius of curvature can be relatively small. For convenience, such parts are referred to throughout the remainder of the description and in the claims under the generic term of "bowls". A field of application of the invention is, for example, manufacturing bowls for receiving crucibles containing molten metal, such as silicon, in particular for drawing ingots of silicon, or of other metals in other metallurgical fields.

The term "thermostructural composite material" is used to mean a material comprising fiber reinforcement made of refractory fibers, e.g. carbon fibers or ceramic fibers, and densified by a refractory matrix, e.g. of carbon or of ceramics. Carbon/carbon (C/C) composite materials and ceramic matrix composite (CMC) materials are examples of thermostructural composite materials.

Background of the invention

A well-known method of producing silicon single crystals in particular for manufacturing semiconductor products consists in melting silicon in a receptacle, in putting a crystal germ having a desired crystal arrangement into contact with the bath of liquid silicon, so as to initiate solidification of the silicon contained in the crucible with the desired crystal arrangement, and in mechanically withdrawing an ingot of single crystal

silicon obtained in this way from the crucible. This method is known as the Czochralski method or as the "Cz" method.

- 5 The receptacle containing the molten silicon is frequently a crucible made of silica or quartz (SiO_2) placed in a bowl, sometimes called a susceptor, which is generally made of graphite. Heating can be provided by radiation from an electrically conductive cylindrical body made of graphite, e.g. heated by the Joule effect, 10 which surrounds the bowl. The bottom of the bowl stands on a support. For this purpose, the bottom of the bowl is generally machined, in particular so as to form a bearing surface for centering purposes and also a support zone. In addition, in the application in question, very 15 high purity requirements make it necessary to use raw materials that are pure, with methods that do not pollute them, and/or with methods of purification in the finished state or in an intermediate state of bowl manufacture. For carbon-containing materials (such as graphite or C/C 20 composites), methods of purification by high temperature treatment (at more than 2000°C) under an atmosphere that is inert or reactive (e.g. a halogen) are known and are commonly used.

- The pieces of graphite used as bowls are fragile. 25 They are often made up of as a plurality of portions (so-called "petal" architecture) and they cannot retain molten silicon in the event of the crucible made of silica leaking or rupturing. This safety problem becomes more critical with the increasing size of the silicon 30 ingots that are drawn, and thus with the increasing mass of the liquid silicon. Furthermore, graphite bowls are generally of short lifetime while being very thick and thus bulky and heavy.

- To avoid these drawbacks, proposals have already 35 been made to make bowls out of C/C composite material. Such a material has much better mechanical strength than graphite. Making bowls of large diameter, e.g. as great

as or even more than 850 millimeters (mm) can then be envisaged in order to deal with the requirement for monocrystalline silicon ingots of larger section. In addition, the thickness of such bowls can be decreased compared with the thickness of graphite bowls, thus improving the transmission of heat flux to the crucible and reducing bulk. Furthermore, C/C composite materials are less exposed than graphite to becoming brittle following corrosion from SiO coming from the crucible.

The manufacture of a C/C composite material piece, or more generally a piece of thermostructural composite material, usually comprises making a fiber preform having the same shape as the piece that is to be made, and that constitutes the fiber reinforcement of the composite material, and then densifying the preform with the matrix.

Techniques presently in use for making preforms include winding yarns by coiling yarns on a mandrel having a shape that corresponds to the shape of the preform that is to be made, draping which consists in superposing layers or plies of two-dimensional fiber fabric on a former matching the shape of the preform to be made, the superposed plies optionally being bonded together by needling or by stitching, or indeed by three-dimensional weaving or knitting.

The preform can be densified in well-known manner using a liquid process, a gas process, or a dual process combining both of them. Liquid process densification consists in impregnating the preform - or in pre-impregnating the yarns or plies making it up - with a matrix precursor, e.g. a carbon or ceramic precursor resin, and in transforming the precursor by heat treatment. Gas densification, known as chemical vapor infiltration, consists in placing the preform in an enclosure and in admitting a matrix-precursor gas into the enclosure. Conditions, in particular temperature and pressure conditions, are adjusted so as to enable the gas

0566862-072504

to diffuse into the core of the pores of the preform, so that on coming into contact with the fibers it forms a deposit of matrix-constituting material thereon by one of the components of the gas decomposing or by a reaction taking place between a plurality of components of the gas.

For pieces that are of hollow shape that cannot be developed, for example pieces that are bowl shaped, a particular difficulty lies in making a fiber preform having the right shape.

The filament-winding technique is very difficult to implement in order to obtain a bowl shape as a single piece. A solution that can be recommended is to make the side wall of the bowl preform by winding a filament and to make the portion of the preform that corresponds to the bottom of the bowl separately.

The technique of draping plies is also difficult to implement for shapes that are this complex when it is desired to avoid forming extra thickness due to folds in the plies. A known solution consists in cutting the plies, in particular to form slots, as a function of the shape that is to be made so that the plies can fit closely on this shape with the lips of the cutouts or slots coming together once draped and shaped. Such plies must be precut with very great precision. Cut plies also present the drawback of leaving discontinuities in the yarns of the preform.

Object and summary of the invention

In one of its aspects, an object of the invention is to propose a method of manufacturing a bowl out of thermostructural composite material making it possible to avoid the drawbacks of the prior art, while remaining simple and low in cost.

According to the invention, the method comprises the steps which consist in:

- providing deformable two-dimensional fiber plies;

- superposing the plies while deforming them on a former having a shape that corresponds to the shape of the bowl to be made, the plies fitting closely on said former by deforming and without forming folds; and

5 - bonding together the deformed plies by means of fibers that extend transversely relative to the plies, so as to obtain a bowl preform which is subsequently densified.

The invention is remarkable in that the bowl preform
10 can be made of unitary plies that do not include any slots for enabling them to fit closely to the desired shape. This contributes to providing better mechanical and cohesive behavior to the bowl obtained by densifying the preform, and to providing a high level of safety in
15 the event of the crucible breaking, in the context of the application to drawing silicon ingots.

The plies are made of deformable fiber fabric. Advantageously, a fabric is used made up of a plurality of unidirectional sheets superposed in different
20 directions, for example two unidirectional sheets superposed with directions at an angle preferably lying in the range 45° to 60° relative to each other, the sheets being bonded together so as to form deformable individual mesh loops. The sheets can be bonded together
25 by needling or by knitted thread or by stitching. Entire plies are cut out to the desired dimensions in the deformable fabric. Plies are thus obtained having a capacity for deformation which is sufficient to enable them to take up the desired shape merely by deforming,
30 without forming folds or increases in thickness.

Advantageously, the deformed plies are bonded to one another by needling, so as to transfer fibers taken from the plies by the needles in a direction that extends transversely relative to the plies. Each new draped ply
35 can be needled onto the underlying structure, advantageously while controlling the density of

BP663862-072304

transferred fibers throughout the thickness of the preform.

In a variant, the deformed sheets can be bonded together by stitching or by implanting threads.

- 5 In another implementation of the method of the invention, the deformable fiber fabric constituting the plies is a knit.

- 10 The fibers constituting the plies are preferably made of carbon or of a carbon precursor. If they are made of precursor, heat treatment is performed after the preform has been made so as to transform the precursor into carbon.

- 15 After the preform has been made, it can be subjected to a step of consolidation by a liquid method, and to heat treatment for stabilizing the fibers and for purification which can be performed after or prior to consolidation.

- The optionally consolidated preform is preferably densified by chemical gas infiltration.

- 20 In a preferred implementation, deformable two-dimensional fiber plies are used that are whole, having no cutouts or slots, so as to obtain a complete bowl preform as a single piece, and densification is performed on the complete bowl preform. A one-piece bowl of
25 thermostructural composite material can thus be obtained directly.

- In another implementation, one-piece deformable two-dimensional fiber plies are likewise used that are free from any cutouts or slots so as to obtain a complete bowl
30 preform, but a hole is made through the bottom of the preform prior to densification by chemical vapor infiltration. The presence of this hole enhances flow of the gas, thereby making it possible to increase densification efficiency, particularly with bowls of
35 large dimensions. After the preform has been densified, at least in part, the hole is closed with a plug. It is possible to use a plug made of thermostructural composite

098962-07201
10220-288880

material. After the hole has been closed by the plug, a final step of densification by chemical vapor infiltration can be performed.

5 In yet another implementation, one-piece two-dimensional fiber plies are used that present a substantially central opening, and the plies are superposed on the former with their openings in alignment so as to obtain a bowl preform presenting a hole passing through the bottom of the preform and constituted by the aligned openings in the plies. After the preform has
10 been densified at least in part by chemical vapor infiltration, the hole is closed by a plug. As mentioned above, the bowl can be made of a thermostructural composite material and a final step of chemical vapor
15 infiltration can be performed.

In any event, once the preform has been densified, a bowl blank is obtained.

Final purification heat treatment can then optionally be performed.
20 In addition, a final deposition of pyrolytic carbon and/or of silicon carbide (SiC) can be performed, at least on the inside face of the bowl.

In another aspect, the invention also provides a bowl of thermostructural composite material of the kind
25 that can be obtained by the above-defined method.

In the invention, such a bowl is characterized in that it comprises fiber reinforcement comprising two-dimensional fiber plies which are superposed and bonded together by fibers extending transversely relative to the
30 plies.

Advantageously, the fiber reinforcement constitutes a single piece made up of one-piece two-dimensional plies free from slots and cutouts.

A coating of pyrolytic carbon can be present on the surface of the bowl, at least on the inside of the bowl.
35

The invention also provides the use of such a bowl as a crucible support, in particular for producing

monocrystalline silicon. A protective layer, e.g. of thermostructural composite material, such as a C-C composite, can be interposed between the bowl and the crucible.

5

Brief description of the drawings

The invention will be better understood on reading the following description given by way of non-limiting indication and made with reference to the accompanying drawings, in which:

10

- Figure 1 is a highly diagrammatic half-section view showing a bowl of composite material used as a crucible support in an installation for producing silicon ingots;

15

- Figure 2 is a flow chart showing the successive steps in a first implementation of a method in accordance with the invention;

- Figures 3A, 3B, and 3C are views showing a two-dimensional ply with deformable mesh loops suitable for implementing the method of Figure 2;

20

- Figure 4 is a highly diagrammatic view of needling apparatus in a form suitable for implementing the method of Figure 2;

- Figure 5 is a fragmentary diagrammatic view showing additional draping of plies over a portion of the bottom of the bowl;

25

- Figure 6 is a flow chart showing successive steps in a second implementation of a method in accordance with the invention;

- Figure 7 is a diagrammatic section view showing a plug closing a hole formed in the bottom of a preform;

30

- Figure 8 is a flow chart showing the successive steps in a third implementation of a method in accordance with the invention; and

- Figure 9 is a highly diagrammatic view showing plies being draped in yet another implementation of a method in accordance with the invention.

35

Detailed description of implementations of the invention

As already mentioned, a non-limiting example to which the invention applies is that of making bowls of thermostructural composite material for supporting crucibles in installations that produce single crystal silicon ingots.

Highly diagrammatic Figure 1 shows such a bowl of composite material, e.g. C/C composite material supporting a crucible 5 which is usually made of silica.

The bowl 1 stands on an annular support formed with a ring 2 mounted at the end of a shaft 3 having a setback 4 therein. The bowl has a bottom portion 1a and a surround portion 1b, part of which is substantially cylindrical and is connected to the bottom portion via a region of rounded profile. The bottom portion of the bowl 1 is machined so as to form a centering bearing surface corresponding to the setback 4 and a support surface on the ring 2.

After the crucible has been filled with silicon, the assembly is placed in a furnace and the temperature in the furnace is raised to a value which is high enough to cause the silicon to liquefy. At this temperature, greater than 1420°C, the silica crucible softens and it matches the shape of the bowl. A germ having a crystal arrangement is then brought into contact with the bath of silicon and an ingot is extracted slowly therefrom, thereby forming a column between the germ and the bath. An ingot can thus be drawn, and its length can lie in the range 1 meter (m) to 2 m.

That method of manufacturing silicon ingots is well known and does not form part of the invention, such that a more detailed description is not required.

Because thermostructural composite materials have the ability to conserve good mechanical properties and good dimensional stability at high temperatures, they are particularly suitable for making bowls for use in the above application.

The description below relates more particularly to making bowls out of C/C composite materials with carbon fiber reinforcement and a carbon matrix, or at least a matrix that is essentially made of carbon. The invention also covers making bowls out of CMC type composite materials, i.e. having ceramic fiber reinforcement (e.g. made of SiC fibers) and a matrix that is also ceramic (e.g. likewise of SiC), where technologies for making CMCs are well known.

The fiber reinforcement can be made from carbon yarns of the kind commercially available, but preferably free from any of the surface treatment normally performed to provide surface functions that encourage bonding with an organic matrix when such yarns are used to form fiber/resin type composite materials that are not intended for high temperature applications. The absence of surface functions makes it possible to avoid internal stresses during the process of manufacturing the composite material using the method of the invention.

In a variant, before or immediately after making the fiber reinforcement, it is possible to subject ordinary commercial carbon yarns to heat treatment seeking to eliminate surface functions, and the fibers constituting the yarns can be provided with a thin interphase coating of pyrolytic carbon, typically having a thickness less than or equal to 0.1 micrometers (μm). The interphase coating of pyrolytic carbon can be obtained by chemical vapor deposition, as described in the Applicants' US patent No. 4 748 079.

A first implementation of the method for manufacturing a composite material bowl is described below with reference to Figure 2.

A first step 10 of the method consists in providing deformable two-dimensional plies of carbon fiber.

The plies are made of a deformable fiber fabric, advantageously made up of unidirectional sheets of carbon yarns having no surface functions, which are superposed

with different directions and bonded together so as to form deformable individual mesh loops.

The sheets can be bonded together by light needling which provides the fabric with cohesion while leaving it with sufficient ability to deform. It is also possible to bond the sheets to one another by stitching using a thread passing from one face to the other of the fabric.

The sheets are preferably bonded together by knitting a thread passing from one face to the other of the fabric, as shown in Figures 3A to 3C. Such deformable fabrics are known and they are described in the Applicants' document WO 98/44182. They are constituted by two unidirectional sheets superposed with the directions between each other making an angle of less than 90°, preferably an angle lying in the range 45° to 60°.

Figures 3A and 3B show the front and back faces of the fabric 102 while Figure 3C shows in greater detail the knitting stitch 108 used. The stitch is in the form of interlaced loops 108a that are elongate in a longitudinal direction of the fabric 102 and that form a plurality of parallel rows, together with V-shaped or zigzag paths 108b which interconnect loops in adjacent rows. The fabric 102 is situated between the paths 108b situated on the front face (Figure 3A) and the loops 108a situated on the back face (Figure 3B), giving the knit the appearance of a zigzag stitch on one face and the appearance of a chain stitch on the other face. The knitting stitch overlies a plurality of yarns in each unidirectional sheet depending on the gauge selected for the knitting machine.

The bridges between the zigzag paths 108b and the loops 108a, such as points A, B, C, and D in Figure 3C define the vertices of the deformable individual mesh loops. Under such circumstances, both the loops defined by the knitting stitch and the loops defined by the cross-points between the threads of the sheets are

deformable, with the cross-points serving to constitute deformable parallelograms.

The knitting thread used 106 can be a carbon thread or a thread made of a carbon precursor, or indeed a thread made of a sacrificial material, i.e. a material that is to be removed by being dissolved or by heat so as to leave no residue at a subsequent stage in the manufacture of the composite bowl. An example of a sacrificial thread is a thread made of polyvinyl alcohol (PVA) that is soluble in water.

The plies are cut out from the deformable fabric to the outside dimensions that are required by the shape and dimensions of the bowl to be made. The plies are whole, constituting single pieces that are free from any internal cutouts or slots.

In the following step 20 of the method, the plies are draped onto tooling having a shape corresponding to the shape of the bowl that is to be made. Draping can be performed manually.

Because the mesh loops of the plies are deformable and because of the way in which the plies are draped, it is possible to give the superposed plies the desired shape without forming any folds, while nevertheless using plies that are whole without any slots or cutouts.

Compared with the technique consisting in forming cutouts in two-dimensional plies that are not sufficiently deformable, e.g. so as to form petals that can fit closely to the desired shape without folds or extra thicknesses, the use of plies having deformable mesh loops presents the advantages of being easier to drape and of preserving the integrity of the structure of the plies. This point is particularly important for the mechanical properties of the final bowl.

The plies are superposed by being offset angularly about the axis of the preform passing through the top thereof, so as to avoid exact superposition of their

patterns, since that can lead to non-uniformity in the structure.

The plies are stacked until the desired thickness has been obtained for the bowl preform, and they are bonded to one another by needling (step 30).

The needling can be performed after the plies have been draped, or preferably as the draping is taking place, e.g. by needling each newly-draped ply.

By way of example, a needling installation is used of the kind described in the Applicants' US patent No. 5 266 217. As shown very diagrammatically in Figure 4, such an installation comprises a table 300 supporting a former 302, a robot 304 having a control unit 306 connected to an operator console 308 and a needling head 310 fixed to the end to the arm 312 of the robot 304. The other end of the arm 312 is hinged about a vertical axis to a vertically movable support 314. In the vicinity of the needling head, the arm 312 has a multi-axis articulation 316.

The needling head 310 thus possesses the degrees of freedom required for being brought into the desired position with the desired orientation for needling the plies draped on the former 302, and to perform needling along preestablished trajectories with a predetermined direction of incidence, generally normal to the plies.

The former 302 is provided with a backing coating, e.g. a felt into which the needles of the head 310 can penetrate without being damaged.

The needling head 310 is provided with a presser plate 310a having perforations through which the needles pass. The presser plate is urged resiliently to exert controlled pressure on the plies being needled.

Advantageously, needling is performed while controlling the density of fibers transferred by the needles transversely relative to the plies. This can be achieved by controlling the penetration depth of the needles so as to obtain needling density that is

substantially constant throughout the thickness of the preform.

The preform 320 constituted by the draped and needled plies 102 is advantageously associated with additional plies being draped (step 40) having dimensions that are restricted to the dimensions of the bottom portion of the bowl that is to be made.

As shown in Figure 5, the additional plies 104 (which can be of the same kind as the plies 102) are draped on the bottom of the preform 320 until sufficient thickness has been obtained to enable the bottom portion of the bowl to be machined so as to form a support face with a centering bearing surface.

The plies 104 are bonded together and to the plies 102 by needling. This is done using a needling installation of the kind described above.

The resulting fiber preform is then subjected to a consolidation process using a liquid.

For this purpose, the fiber preform 54 is placed in a mold 56 and impregnated with a liquid precursor of carbon (step 50). Impregnation can be performed using a phenolic resin, for example.

After the resin has been polymerized in the mold, the preform is removed from the mold and is subjected to heat treatment to carbonize the resin.

In a variant, impregnation can be performed on the preform while it is maintained on the former, after needling. For this purpose, the resin is inserted into the preform while it is covered in a flexible cover, e.g. made of elastomer, possibly associated with suction. The cover can then be withdrawn and the preform removed, after the resin has polymerized and before it is carbonized.

The following step 60 of the method consists in performing heat treatment to stabilize the carbon fibers dimensionally and to purify the consolidated preform. The heat treatment is performed at a temperature that

preferably lies in the range 1600°C to 2800°C. It serves to prevent subsequent dimensional variation of the fibers during continued manufacture of the bowl when the fibers have not previously been exposed to a temperature not less than that to which they are exposed subsequently, in particular during densification. This encourages removal of the impurities contained in the fibers and in the coke of the consolidation resin.

Thereafter, the preform is densified by a matrix of pyrolytic carbon using chemical vapor infiltration (step 70). To this end, in well-known manner, the preform can be placed in an enclosure into which a gas is introduced that contains a precursor of carbon, e.g. methane. The pressure and temperature conditions are selected in such a manner as to enable the gas to diffuse within the pores of the consolidated preform, and to enable the methane to decompose so as to give a deposit of pyrolytic carbon.

Chemical vapor infiltration can be implemented under constant-temperature, constant-pressure conditions, or with a temperature gradient, both of which processes are well known.

Infiltration can also be performed by immersing the consolidated preform in a liquid precursor and by heating the preform so as to develop a film of gaseous precursor at its surface. Such a method is described, for example in the Applicants' document FR 2 784 695.

In another variant, the preform can be densified using a liquid in the form of a precursor for the matrix, e.g. a resin.

After densification, the resulting bowl blank is machined (step 80) in particular for the purpose of forming the centering bearing surface and the support surface at the bottom of the bowl.

A final heat treatment step is performed (step 90) e.g. at a temperature in the range 2200°C to 2700°C in order to purify the resulting C/C composite bowl. In

conventional manner, the purification treatment can be performed in the presence of a halogen.

5 A final deposit of pyrolytic carbon (step 100) can be performed by chemical vapor deposition. This deposit is formed on the surface of the bowl, at least on the inside. In variant, this final deposit can be of silicon carbide (SiC), likewise obtained by chemical vapor deposition.

10 The final deposition of pyrolytic carbon or of SiC could alternatively be performed prior to the final purification heat treatment.

Another implementation of the method of the invention is described below with reference to Figures 6 and 7.

15 The method whose successive steps are shown in Figure 6 has the same initial steps 10 to 60 as the method of Figure 2, i.e. supplying deformable two-dimensional fiber plies (step 10), draping the plies on a former (step 20), bonding the draped plies together by needling (step 30), draping additional plies (step 40), impregnating with a resin for consolidation purposes (step 50), and stabilization and purification heat treatment (step 60).

25 Thereafter, the method of Figure 6 differs from that of Figure 2 in that prior to densifying the preform, a hole 52 is machined through the bottom of the consolidated preform 58 (step 65). It should be observed that the hole 52 can be formed in the non-consolidated preform prior to impregnation with the resin, or
30 immediately after the resin has been polymerized but prior to the resin being carbonized.

The presence of the hole 52 can be beneficial during densification of the preform by chemical vapor infiltration. The hole 52 encourages flow of the gas
35 through the enclosure in which the preform is placed.

Step 70 of densifying the preform is thus preferably performed by chemical vapor infiltration.

The preform densified in this way is machined (step 80) in particular the bottom of the preform is machined.

A plug is then made (step 82) for inserting in the hole 52 (step 86).

- 5 The plug can be made of various different materials, e.g. of graphite, or preferably of a thermostructural composite material such as a C/C composite. The plug can be made as one or more parts that are obtained by densifying one or more corresponding preforms. The or
- 10 each preform is formed by superposing two-dimensional plies, e.g. of woven fabric, which are bonded together by needling or by stitching. Densification by means of a carbon matrix is then performed using a liquid or by chemical vapor infiltration. In the example shown in
- 15 Figure 7, the plug 84 comprises two parts 84a and 84b. The part 84a is cup-shaped with a lip-shaped outline that bears against a setback 52a formed in the wall of the hole 52 on the inside of the bowl preform. The outside
- 20 face of the part 84a is of a shape that fits continuously with the inside face of the bowl. The part 84b is also cup-shaped with an outline in the form of a lip which bears against the outside face of the bottom of the preform of the bowl around the hole 52. The parts 84a and 84b can be bonded together by screw fastening, with
- 25 the part 84a having a projecting central portion which is screwed into a housing in the part 84b. The parts 84a and 84b are thus clamped to the rim of the hole 52.

- After the plug has been put into place, a new step 88 of chemical vapor infiltration can be performed so as
- 30 to complete assembly of the plug 84 with the bottom portion of the bowl preform and so as to finish off densification. The densification performed in step 80 could then have been performed in partial manner.

- Steps 90 and 100 of final heat treatment for
- 35 purification and for depositing pyrolytic carbon can then be performed as in the method of Figure 2.

Yet another implementation of the method of the invention is briefly described with reference to Figure 8.

5 This method comprises steps 10 to 100 that are the same as the method of Figure 2 with the exception of steps 30 and 40 of bonding draped plies and of draping additional plies.

10 In the method of Figure 8, plies 102 are bonded to one another (step 30') by stitching using a thread 202 which passes through the set of draped plies 102. A similar thread 204 is used in the following step 40' to bond additional plies 104 to one another and to the plies 102, with the thread 204 passing through all of the plies 102 and 104.

15 The threads 202 and 204 can be carbon threads similar to those used for forming the plies 102 and 104. In a variant, it is possible to use threads of a sacrificial material, i.e. a material suitable for being eliminated by being dissolved or by heat at a subsequent stage in preparation of the bowl.

20 It is also possible to bond the plies 102 together by stitching and to bond the plies 104 together and to the plies 102 by needling, as in step 40 of Figure 6.

25 It should also be observed that the method of bonding the plies 102 and 104 together by stitching could be used instead of the needling technique used in the method of Figure 6.

In yet another implementation of the method of the invention, deformable two-dimensional plies are used that present a substantially central opening.

30 As shown in Figure 9, the plies 202 provided with a central opening 203 are draped on a former, e.g. the same former 302 as is shown in Figure 4. The plies 202 are draped so that the openings 203 are in alignment in the central portion of the bottom of the preform that is being built up.

The plies 202 are bonded together by needling, as in the methods of Figures 2 and 6, or by stitching as in the method of Figure 6.

Additional plies 204 are draped on the bottom of the preform, the plies 204 having substantially central openings 205 that are in alignment. The plies 204 are bonded to one another and to the plies 202 by needling or by stitching.

The aligned openings 203, 205 define a hole 152 passing through the bottom of the preform.

After the plies 202 and 204 have been draped and bonded together, manufacture of the bowl can continue with steps of consolidation by resin impregnation, stabilization and purification heat treatment, densification by chemical vapor infiltration, machining, preparing and installing a plug closing the hole 152, final densification by chemical vapor infiltration, purification heat treatment, and deposition of pyrolytic carbon, as in steps 50, 60, 70, 80, 82, 86, 88, 90, and 100 of the method of Figure 6.

Other variants can be applied to the method described above without going beyond the ambit of the protection defined by the accompanying claims. Thus, the preform can be made out of yarns made of carbon precursor fibers instead of carbon fibers. Suitable carbon precursors include, in conventional manner, preoxidized polyacrylonitril (PAN), phenolic compounds, and pitch. The precursor is transformed into carbon by heat treatment after the preform has been built up.

The stage of consolidating the preform could be omitted. The preform with the superposed and bonded-together plies could then be placed in tooling of a shape corresponds to the shape of the bowl to be made so as to be inserted in an enclosure for densification by chemical vapor infiltration. The tooling can be withdrawn after a first densification stage that provides sufficient

cohesion to enable densification to be continued without tooling.

The stage of heat treating the preform prior to densification could be omitted, in particular when the fibers do not need to be stabilized dimensionally. This can be the case when the carbon fibers of the preform have already been raised to a temperature not less than the temperature encountered subsequently. Purification can then be performed in a single operation after densification.

Alternatively, the final purification stage could be omitted, providing the degree of purity obtained for the preform by the heat treatment prior to densification, and when densification is performed with a carbon precursor under conditions that do not introduce significant quantities of impurities. When a high level of purity needs to be complied with for the material contained in the crucible supported by the manufactured bowl, as is the case for silicon that is for use in manufacturing semiconductors, the level of residual impurities in the bowl must preferably be below 5 parts per million (ppm).

In addition, the preform could be densified using a matrix that is made at least in part out of a ceramic material, e.g. silicon carbide obtained by chemical vapor infiltration and using a gas precursor such as methyltrichlorosilane.

Finally, although the description above relates to forming a coating of pyrolytic carbon or of SiC particularly on the inside face of the bowl, other forms of protection could be adopted, instead of or as well as a coating of pyrolytic carbon or of SiC.

In particular, a protective layer could be interposed between the bowl and the crucible, to avoid attacking the composite material of the bowl, as can happen with a crucible made of silica and a bowl made of C/C composite material.

By way of example, the protective layer can itself be made of a thermostructural composite material, such as a C/C composite and it can behave as a "consumable" layer that needs to be replaced periodically. The C/C

5 composite material used can be made up of two-dimensional plies of carbon fibers bonded together by a matrix of carbon obtained by using a liquid or chemical vapor infiltration.

10 Such a protective layer 6 fitting closely to the shape of the inside surface of the bowl 1 is shown in Figure 1.

2025-07-20 10:20:20

CLAIMS

- 1/ A method manufacturing bowl of thermostructural composite material formed by fiber reinforcement densified by a matrix, the method comprising making a
- 5 preform constituting the fiber reinforcement by draping two-dimensional fiber plies on a former of shape corresponding to the shape of the bowl to be made, and densifying the preform with a material constituting the matrix of the composite material,
- 10 the method being characterized by using deformable two-dimensional fiber plies, superposing said plies on the former, deforming the plies so that the plies fit closely on said former by deforming without forming folds, and bonding the superposed plies to one another by
- 15 means of fibers extending transversely relative to the plies so as to obtain a one-piece bowl preform which is subsequently densified.
- 2/ A method according to claim 1, characterized in that
- 20 plies are used made of a fabric formed of a plurality of unidirectional sheets superposed in different directions and bonded together so as to form deformable individual mesh loops.
- 25 3/ A method according to claim 2, characterized in that plies are used made of a fabric formed of two unidirectional sheets superposed with directions that are at an angle of 45° to 60° between each other.
- 30 4/ A method according to claim 2 or claim 3, characterized in that the unidirectional sheets are bonded to one another by knitting a thread which passes from one side of the fabric to the other.
- 35 5/ A method according to claim 2 or claim 3, characterized in that the unidirectional sheets are bonded together by needling.

10080502-072301

- 6/ A method according to claim 2 or claim 3,
characterized in that the unidirectional sheets are
bonded together by stitching with a thread that passes
5 from one side of the fabric to the other.
- 7/ A method according to any one of claims 2 to 6,
characterized in that the plies are superposed by being
mutually angularly offset around an axis passing through
10 the bottom of the bowl.
- 8/ A method according to claim 1, characterized in that
deformable fiber plies are used that are formed by
knitting.
- 15 9/ A method according to any one of claims 1 to 8,
characterized in that plies are used formed of carbon
fiber yarns that are free of surface functions.
- 20 10/ A method according to any one of claims 1 to 8,
characterized in that plies are used formed of carbon
fiber yarns provided with an interphase coating of
pyrolytic carbon.
- 25 11/ A method according to any one of claims 1 to 10,
characterized in that the superposed plies are bonded
together by needling so as to transfer fibers taken from
the plies transversely thereto.
- 30 12/ A method according to claim 11, characterized in that
each newly draped ply is needled onto the underlying
structure.
- 13/ A method according to any claim 11 or claim 12,
35 characterized in that the density of fibers transferred
transversely relative to the plies is controlled
throughout the thickness of the preform.

0365852-072234

14/ A method according to any one of claims 1 to 10, characterized in that the superposed plies are bonded together by stitching.

5

15/ A method according to any one of claims 1 to 10, characterized in that the superposed plies are bonded together by implanting threads transversely relative to the plies.

10

16/ A method according to any one of claims 1 to 15, characterized in that the preform is consolidated prior to densification.

15

17/ A method according to claim 16, characterized in that the preform is consolidated by being impregnated with a resin, by polymerizing the resin, and by carbonizing the polymerized resin.

20

18/ A method according to any one of claims 1 to 17, characterized in that, prior to densification, the preform is subjected to heat treatment for dimensional stabilization and for purification at a temperature lying in the range 1600°C to 2800°C.

25

19/ A method according to any one of claims 1 to 18, characterized in that the preform is densified by chemical vapor infiltration.

30

20/ A method according to any one of claims 1 to 19, characterized in that the deformable two-dimensional fiber plies used are whole, being free from any cutouts or slots, thereby obtaining a preform for a complete bowl in one piece, and densification is performed on the

35

complete bowl preform.

00000000.072301

21/ A method according to any one of claims 1 to 19, characterized in that the deformable two-dimensional fiber plies used are whole, being free from cutouts or slots, so as to obtain a complete one-piece bowl preform, a hole is made through the bottom of the preform prior to densification of the preform by chemical vapor infiltration, and the hole is subsequently closed by a plug.

22/ A method according to any one of claims 1 to 19, characterized in that the deformable two-dimensional fiber plies used are whole, having a substantially central opening, the plies are superposed on the former so that their openings are in alignment, thereby obtaining a bowl preform with a hole through the bottom of the preform constituted by the aligned openings in the plies, the preform is densified by chemical vapor infiltration, and the hole is subsequently closed by a plug.

23/ A method according to claim 21 or claim 22, characterized in that a plug of thermostructural composite material is used.

24/ A method according to any one of claims 21 to 23, characterized in that an additional step of chemical vapor infiltration is performed after the plug has been put into place in the hole formed in the bottom of the preform.

25/ A method according to any one of claims 1 to 24, characterized in that after densification, purification heat treatment is performed at a temperature lying in the range 1600°C to 2700°C.

26/ A method according to any one of claims 1 to 25, characterized in that after densification, a coating of pyrolytic carbon is formed on the bowl.

5 27/ A method according to any one of claims 1 to 25, characterized in that after densification, a coating of silicon carbide is formed on the bowl.

10 28/ A method according to any one of claims 21 to 27, characterized in that the inside face of the bowl is lined with a protective coating.

15 29/ A method according to claim 28, characterized in that a protective coating is used made of a thermostructural composite material.

20 30/ A bowl of thermostructural composite material formed by fiber reinforcement densified by a matrix, in which the fiber reinforcement comprises superposed two-dimensional fiber plies, the bowl being characterized in that the fiber plies are bonded together by fibers extending transversely relative to the plies.

25 31/ A bowl according to claim 30, characterized in that it is a one-piece bowl and has two-dimensional reinforcing plies that are whole, without cutouts or slots.

30 32/ A bowl according to claim 30 or claim 31, characterized in that the fiber plies are formed of unidirectional sheets superposed in different directions.

35 33/ A bowl according to claim 32, characterized in that the fiber plies are made of carbon fibers.

00000000-072001

34/ A bowl according to claim 33, characterized in that the matrix is formed at least in part out of pyrolytic carbon.

5 35/ A bowl according to claim 33 or claim 34, characterized in that the matrix is made at least in part out of ceramic.

10 36/ A bowl according to claim 35, characterized in that the matrix is made at least in part out of silicon carbide.

15 37/ A bowl according to any one of claims 30 to 36, characterized in that at least its inside face is coated in a layer of pyrolytic carbon.

20 38/ A bowl according to any one of claims 30 to 36, characterized in that at least its inside face is coated in a layer of silicon carbide.

25 39/ The use of a bowl according to any one of claims 30 to 38 for supporting a crucible in an installation for producing monocrystalline silicon ingots, the use being characterized in that a protective layer is interposed between the bowl and the crucible.

40/ A bowl according to claim 39, characterized in that a protective layer of thermostuctural composite material is used.

30

A B S T R A C T

A method of manufacturing a thermostructural composite material bowl, a bowl as obtained by the method, and use of the bowl as a crucible support

A method manufacturing a one-piece bowl of thermostructural composite material comprising fiber reinforcement densified by a matrix. The method comprises supplying deformable fiber plies that are whole, being free from slots or cutouts, superposing said plies on a former of shape corresponding to the bowl to be made, deforming the plies, and bonding the superposed plies to one another by means of fibers extending transversely relative to the plies, e.g. by needling so as to obtain a bowl preform which is then densified. The bowl (1) can be used as a support for a crucible (5) in an installation for producing monocrystalline silicon.

Translation of the title and the abstract as they were when originally filed by the Applicant. No account has been taken of any changes that may have been made subsequently by the PCT Authorities acting ex officio, e.g. under PCT Rules 37.2, 38.2, and/or 48.3.

FIG.1

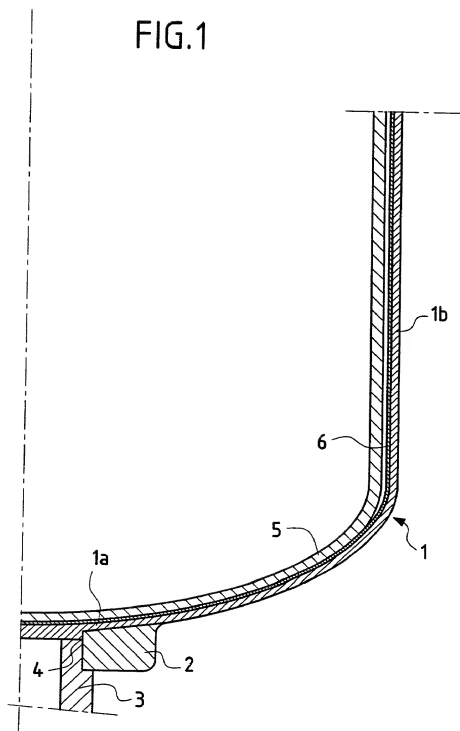
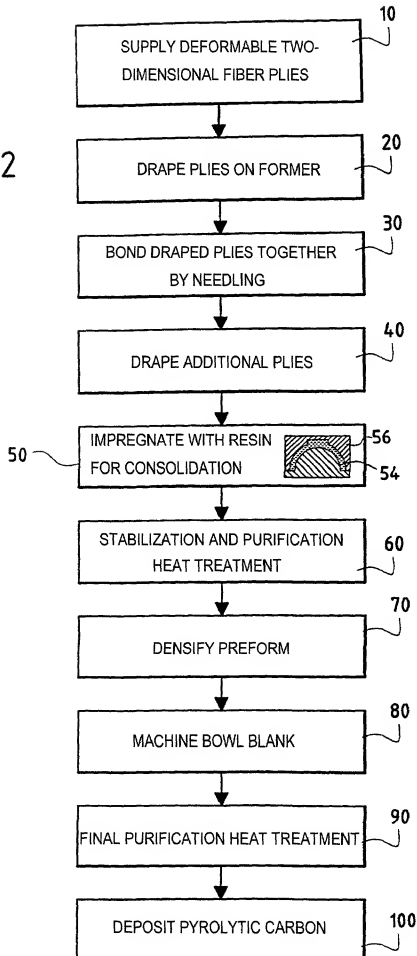


FIG.2



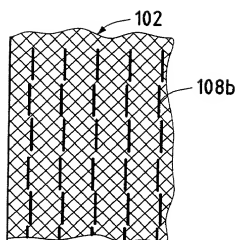


FIG. 3A

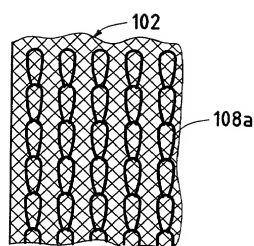


FIG. 3B

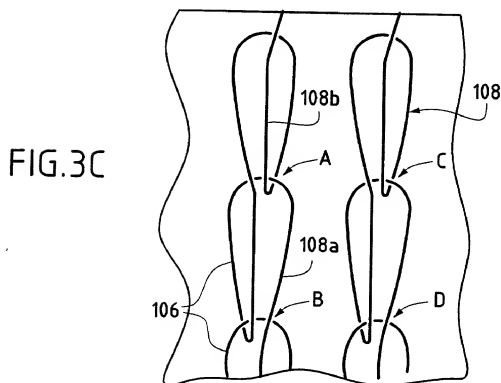
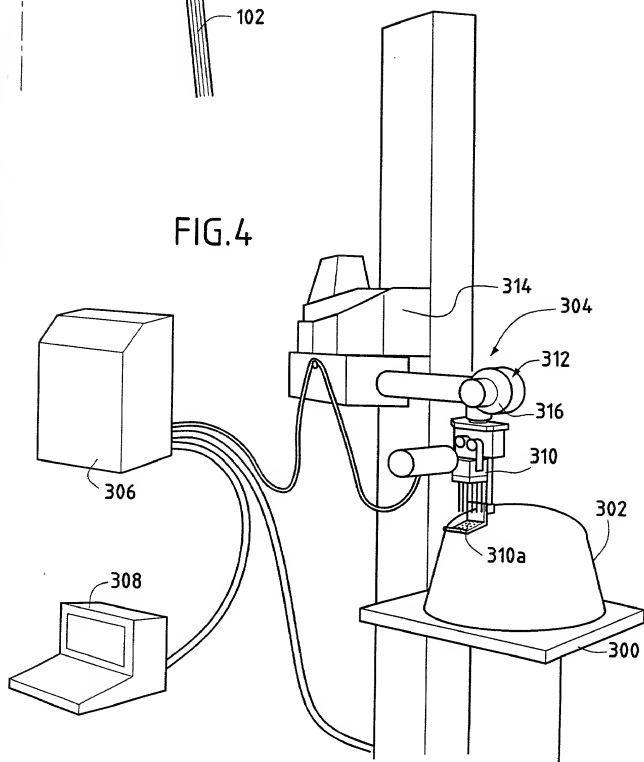
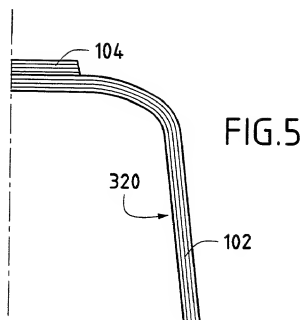


FIG. 3C





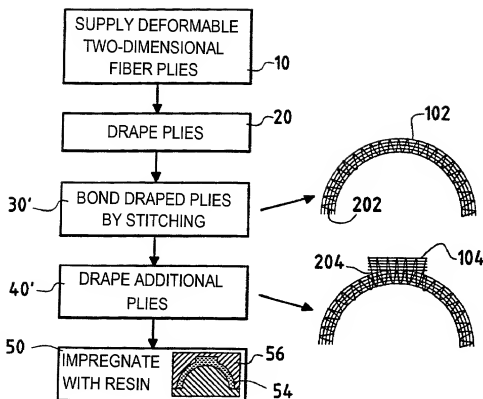
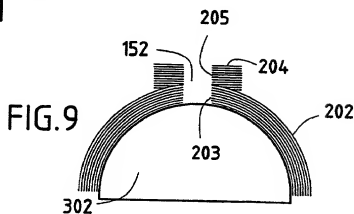
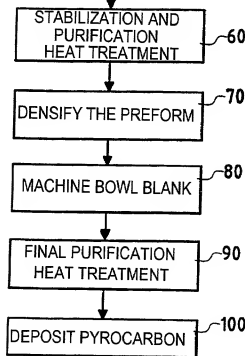


FIG. 8



DECLARATION AND POWER OF ATTORNEY

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the inventor entitled: **A METHOD OF MANUFACTURING A THERMOSTRUCTURAL COMPOSITE MATERIAL BOWL,**

A BOWL AS OBTAINED BY THE METHOD, AND USE OF THE BOWL AS A CRUCIBLE SUPPORT.

the specification of which (check one):

☐ is attached hereto. ☐ was filed _____ as Application No. _____
amended on _____ (if applicable).

☒ was filed as PCT International Application No. **PCT/FR00/03276** on **November 24, 2000**
and was amended under PCT Article 19 on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations §1.56(a).

I hereby claim foreign priority benefits under Title 35, USC §119(a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

<u>Prior Foreign Application(s)</u>	<u>Date Filed</u>	<u>Priority Claimed</u>
99 14766 FRANCE	24/11/1999	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
(Number) (Country)	(Day/Month/Year)	
00 10564 FRANCE	11/08/2000	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
(Number) (Country)	(Day/Month/Year)	

I hereby claim the benefit under Title 35, USC §119(e) of any United States provisional application(s) listed below:

(Application Number)	(Filing Date)
(Application Number)	(Filing Date)
(Application Number)	(Filing Date)
(Application Number)	(Filing Date)

Express Mail Number

EL 751779451 US

I hereby claim the benefit under Title 35 USC §120 of any United States application(s) listed below and insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35 USC §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application No.)	(Filing Date)	(Patented/pending/abandoned)
(Application No.)	(Filing Date)	(Patented/pending/abandoned)
(Application No.)	(Filing Date)	(Patented/pending/abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) to prosecute this application and transact all business connected therewith in the Patent and Trademark Office, and to file with the USRO any International Application based thereon.

Stanley M. Schurgin, Reg. No. 20,979

Charles L. Gagnebin III, Reg. No. 25,467

Paul J. Hayes, Reg. No. 28,307

Victor B. Lebovici, Reg. No. 30,864

Eugene A. Feher, Reg. No. 33,171

Beverly E. Hjorth, Reg. No. 32,033

Holliday C. Heine, Reg. No. 34,346

Gordon R. Moriarty, Reg. No. 38,973

Address all correspondence to:

WEINGARTEN, SCHURGIN, GAGNEBIN & HAYES LLP

Ten Post Office Square


Boston, Massachusetts 02109

Telephone: (617) 542-2290

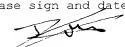
Telecopier: (617) 451-0313


Customer No. 00000000

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and, further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full Name of Sole/First Inventor: <u>GUIRMAN Jean-Michel</u>		
City of Residence <u>BEGLES</u> <u>FR</u>	State or Country <u>FRANCE</u>	Country of Citizenship <u>FRANCE</u>
Post Office Address <u>41 rue de Peyron</u>	City <u>33130 BEGLES</u>	State or Country Zip Code <u>FRANCE</u>
Signature: (Please sign and date in permanent ink.) X 		Date signed: X <u>28 JUNE 2001</u>

Attorney
Docket No.: BDL-352XX

Full Name of Second Joint Inventor: <u>COUPE Dominique</u>		
City of Residence <u>LE HAILLAN</u> FRX	State or Country FRANCE	Country of Citizenship FRANCE
Post Office Address 70 avenue de Paris Parc Ste Christine	City 33185 LE HAILLAN	State or Country Zip Code FRANCE
Signature: (Please sign and date in permanent ink.) X 		Date signed: X 28 JUNE 2001

Full Name of Third Joint Inventor: <u>GEORGES Jean-Michel</u>		
City of Residence <u>BLANQUEFORT</u> FRX	State or Country FRANCE	Country of Citizenship FRANCE
Post Office Address 96 rue de Linas	City 33290 BLANQUEFORT	State or Country Zip Code FRANCE
Signature: (Please sign and date in permanent ink.) X 		Date signed: X 28 JUNE 2001

Full Name of Fourth Joint Inventor:		
City of Residence	State or Country	Country of Citizenship
Post Office Address	City	State or Country Zip Code
Signature: (Please sign and date in permanent ink.) X		Date signed: X